Thermochimica Acta, 187 (1991) 151–158
Elsevier Science Publishers B.V., Amsterdam

KINETIC EVALUATION OF EXOTHERMAL REACTIONS MEASURED BY DSC

E. Kaisersberger and J. Opfermann

NETZSCH Gerätebau GmbH, P.O.Box 1460, D-8672 Selb, Germany

ABSTRACT

Kinetic parameters for two types of exothermal reaction have been determined applying a new software program for multiple curve as well as multiple reaction step analysis. The exothermal deflagration of hexogen (cyclo-1,3,5-trimethylene-2,4,6-trinitramine, RDX), measured by heat flux DSC at four different heating rates (2.5 to 20 K/min), was identified as a consecutive two step reaction. The first step of n-th order type showed the activation energy $E = 193 \pm 3$ kJ/mol, the second reaction step of first order type with autocatalytic contribution showed $E = 186 \pm 2$ kJ/mol.

The vulcanization of a synthetic rubber (EPDM) was measured at five different heating rates (1 to 20 K/min). The exothermal DSC-curves could be best approximated by a two step reaction model of consecutive n-th order reactions. The activation energy of the main step is $E = 180 \pm 3$ kJ/mol, the second step is a superimposed endothermal reaction with $E = 16.6 \pm 3.5$ kJ/mol.

The perfect agreement between recalculated and experimental curves and the degree of conversion of the samples at different time and temperature correlations are shown.

INTRODUCTION

The characteristic data for the description of exothermal reactions are heat production and reaction rate (1). With some limitations, heat production can be measured by DSC easily. The information on reaction rate is not achieved directly from the measurement, but by kinetic evaluations. The aims of kinetic evaluations are optimization of technical processes (improvement of reaction rates), thermal hazard evaluations (safety predictions, e.g. ASTM E 698) and improvement of catalyst or inhibitor functions.

Especially the safe operation of chemical reactors with strongly exothermal reactions requires predictions which are based on the most adequate reaction models. These models must fit all results achieved with different experimental conditions. For this purpose a complex reaction kinetic software program was developed to apply selected multiple step reaction models simultaneously to several heating experiments, covering a broad range of heating rates. With such a "global" kinetic analysis a much higher reliability of the calculated kinetic parameters must be expected compared to evaluations based on only one

0040-6031/91/$03.50

dynamic or on a few isothermal experiments. This expectation was confirmed by kinetic evaluations of TG measurements of irreversible processes (2).

Two different types of exothermal process have been selected for the kinetic evaluations: firstly the exothermal decomposition of an organic material, hexogen, which is representative of a group of chemical hazards with the safety risk of uncontrollable temperature and pressure increase in a reactor vessel during a thermal runaway process; secondly the vulcanization of a synthetic rubber mixture as an example of a commercially important technical process to achieve desired material properties. Safety predictions in the chemical industry as well as process optimization, e.g. in polymer engineering, are of great economic importance.

EXPERIMENTAL

A heat flux DSC (NETZSCH model DSC 200) was used for the determination of the exothermal heat of reaction for the decomposition of hexogen (technical grade explosive) and for the heat of vulcanization of ethylene-propylene-diene rubber (EPDM) by peroxide vulcanization.

Hexogen (cyclo-1,3,5-trimethylene-2,4,6-trinitramine), a highly brisant explosive, was tested in sealed aluminium crucibles with a pinhole in the lid to prevent pressure build up in the crucible during the decomposition. Sample weights of 1.2 mg to 2.1 mg were used. EPDM was tested in sealed aluminium crucibles to prevent evaporation of low boiling plasticizers and accelerators. No weight loss was detected for the vulcanization of samples in the range 5 mg to 12.2 mg.

RESULTS AND DISCUSSION

Hexogen decomposition.

Hexogen shows a melting effect at 206°C (peak temperature) which is immediately followed by the exothermal decompositon. As the gases produced are easily evolved through the pinhole of the crucible lid, the decomposition is detected as a comparably slow deflagration reaction in the range 205°C to 270°C.

The melting heat of 135.6 J/g agrees well with literature (3), the exothermal deflagration heat of 1731 J/g is only about 30% of the heat of explosion (4). This is the expected result for the chosen experimental set-up.

The comparison of the DSC curves at 2.5, 5, 10 and 20 K/min shows a shift of the decomposition peak temperature from 224.2°C to 249.4°C with increasing heating rate (Fig. 1).

The decomposition peak shape indicates a complex reaction, which is also confirmed by the application of a Friedman analysis, i.e. the plot of the logarithm of the conversion rate against 1/T for the four heating curves, taken at various degrees of conversion between
2 % and 95 %. This estimation of the activation energy without assumption of a reaction model shows a variation of the activation energy between 173 kJ/mol and 196 kJ/mol, depending on the degree of conversion. For the simultaneous approximation of the four heating curves with the same reaction model a two-step reaction was chosen. In the iterative non-linear regression, best results were achieved with an initial n-th order reaction followed by a first order reaction with autocatalytic influence. The kinetic parameters are shown in

Table 1. The main contribution to the total conversion is given by the second reaction step of first order with autocatalytic effect.

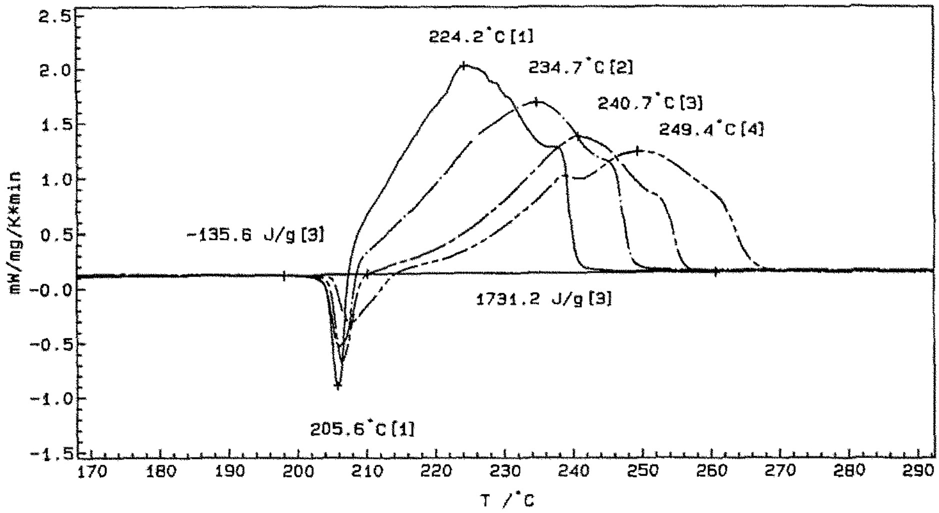

Fig. 1 Hexogen melting and decomposition, heating rates 2.5, 5, 10 and 20 K/min

Table 1
Kinetic parameters for the deflagration of hexogen (RDX)

$$A \xrightarrow{F_n} B \xrightarrow{C_1} C$$

log (A.s) = 17.8 ± 0.3 E = 193 ± 3 kJ/mol n = 0.81 ± 0.07	log (A.s) = 15.3 ± 0.6 E = 186 ± 2 kJ/mol log Kcat = 2.3 ± 0.88 contribution 92.4 %

The excellent agreement between calculated DSC curves (lines) and the experiments (squares) is shown in Fig. 2.

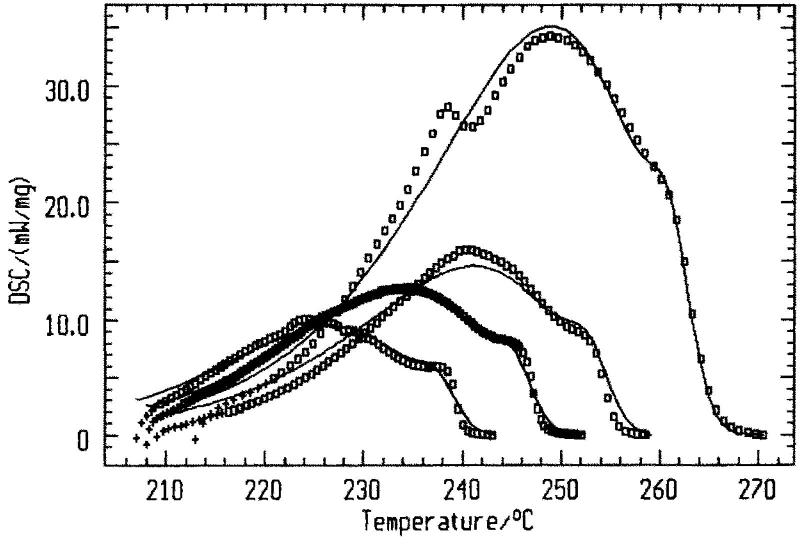

Fig. 2 Simultaneous approximation of four DSC heating curves for the deflagration of hexogen using the kinetic parameters of table 1.

A comparison of kinetic parameters for the decomposition of hexogen is given in Table 2.

Table 2
Comparison of kinetic results for the hexogen decomposition measured by DSC

	E (kJ/mol)	log (A.s)	n	log Kcat
Friedman analysis	172 - 196	16 - 18	-	--
Ozawa-Flynn-Wall	193 - 354	17 - 35	--	--
Netzsch Multiple scan	E1 193 ± 3	17.8 ± 0.3	0.81 ± 0.07	--
	E2 186 ± 2	15.3 ± 0.6	1	2.3 ± 0.88
Dr. Krien (4)	180	--	--	--

Depending on the calculation method applied, the kinetic parameters for the decompositon of hexogen are found in the range 170 to 200 kJ/mol. Values given in literature up to 300 kJ/mol and higher cannot be confirmed, taking the total conversion range of the decomposition of hexogen for the calculation of the kinetic parameters.

The prediction of the stability of a material exposed to higher temperature at prolonged time can be based on kinetic results, if the selected reaction models lead to an adequate mathematical approximation of several heating curves.

Multiple scan and multiple step analysis also offer a calculation of intermediate products (concentration) for isothermal treatment of a sample.

Fig. 3 shows the long term decomposition of hexogen at 190°C over ten hours and the production of the intermediate component B as well as the final product C.

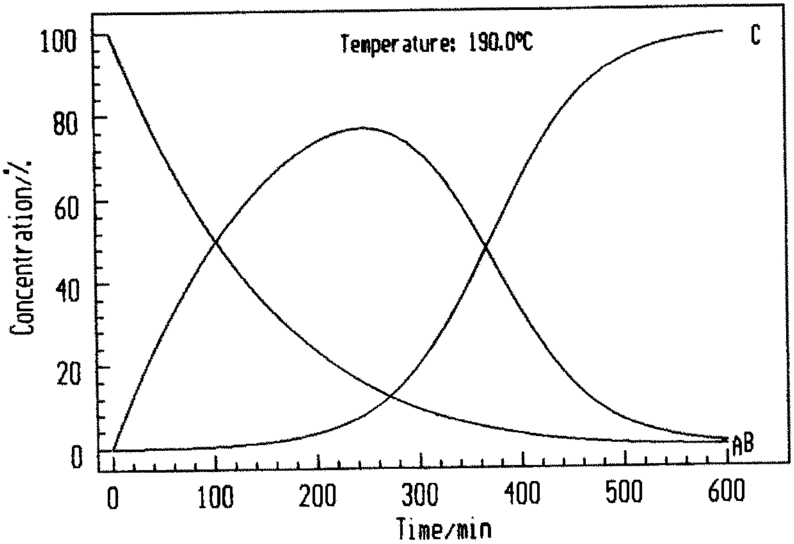

Fig. 3 Decomposition of hexogen at 190°C over ten hours with change of concentration of starting material A, intermediate product B and final product C.

Krien (4) reports in a literature survey that hexogen decomposition starts below the melting range in the gas phase. Therefore the self-generated atmosphere around the sample material has a rate determining function, especially in DSC experiments.

EPDM Curing

Ethylene-propylene rubber with a few percent diene monomer addition is vulcanized by peroxides or also by conventional sulphur vulcanization. The technical rubber mixture for the following kinetic analysis was cured by peroxides at five different heating rates 1, 2, 5, 10 and 20 K/min. The exothermal curing reaction was detected between 120°C and 220°C with a shift of the peak temperature from 173 °C to 200°C with increasing heating rate. Fig. 4 shows the exothermal vulcanization peaks for 2, 5, 10 and 20 K/min.

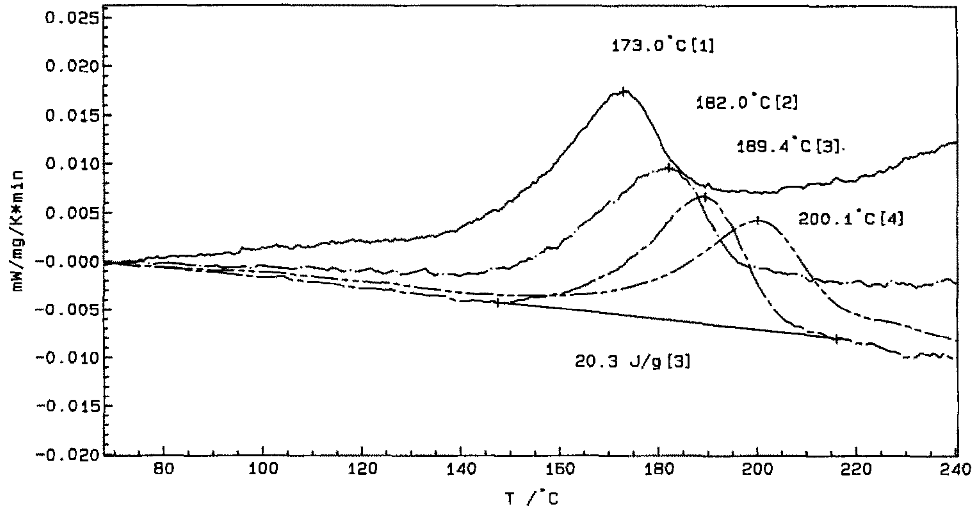

Fig. 4 Vulcanization of EPDM rubber at heating rates of 2, 5, 10 and 20 K/min

The Friedman and Ozawa-Flynn-Wall analysis show for EPDM a variation of the activation energy between 133 kJ/mol and 161 kJ/mol, depending on the degree of conversion. A two-step reaction model of consecutive n-th order reactions was applied for the global kinetic analysis. The resulting kinetic parameters are given in Table 3.

Table 3
EPDM curing

$$A \xrightarrow{F_n} B \xrightarrow{F_n} C$$

log (A.s) = 18.8 ± 0.3	log (A.s) = 0.42
E1 = 180 ± 3 kJ/mol	E2 = 16.6 ± 3.5 kJ/mol
n = 1.01 ± 0.02	n = 0.76 ± 0.03
	contribution - 41 %

The contribution of the second reaction step to the total conversion for the vulcanization is negative, which is interpreted as an overlapping endothermal reaction (e.g.vaporization). Fig. 5 shows the excellent approximation of the five DSC heating curves by the calculated data.

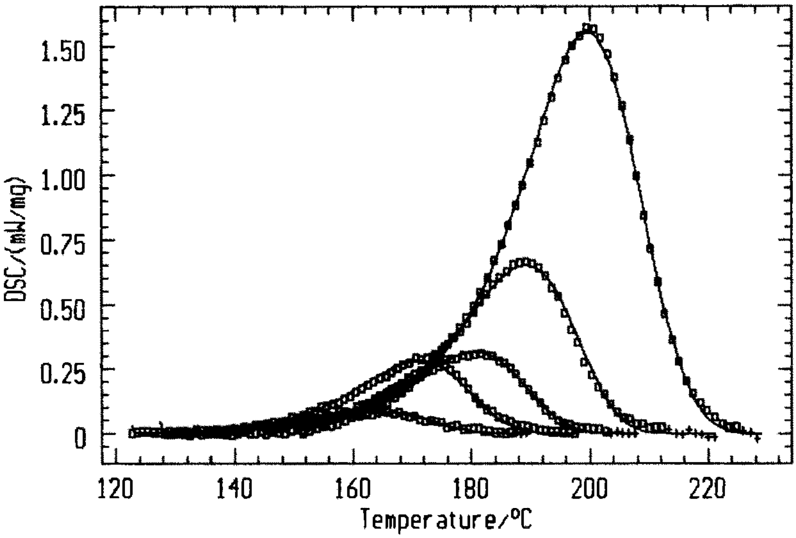

Fig. 5 Simultaneous approximation of five DSC heating curves for the vulcanization of EPDM rubber using the kinetic parameters of Table 3.

The isothermal curing behaviour of EPDM can be predicted by engineering graphics for selectable temperature/time correlations. An example is shown in Fig.6 for the range 130°C to 180°C, which is of technical interest.

Optimization of technical processes as well as information on the safety of chemical reactions can easily be drawn from engineering graphics provided by the kinetic software.

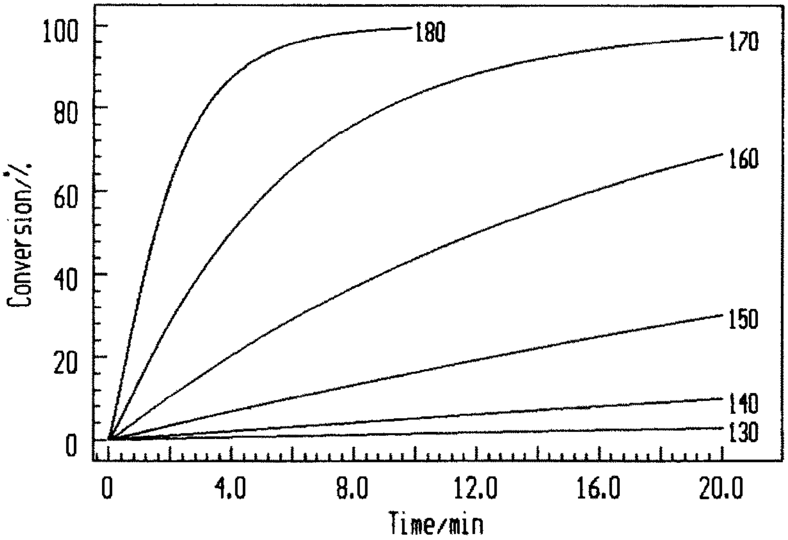

Fig. 6 Isothermal curing behaviour of EPDM (calculated from kinetic parameters of Table 3).

CONCLUSION

Even complex reaction behaviour in solid state reactions can be evaluated by the newly developed kinetic software program. The simultaneous treatment of up to five heating curves, covering a broad range of heating rates, leads to a higher reliability of the evaluated kinetic parameters and allows a more precise prediction of safety and lifetime limits and reaction behaviour in technical processes. The function of the mathematical approximation of DSC curves for exothermal reactions was demonstrated for the decomposition of the explosive hexogen and for the vulcanization of an EPDM rubber.

REFERENCES

1. T. Grewer, O. Klais: Exotherme Zersetzung, Untersuchung der charakteristischen Stoffeigenschaften VDI Verlag, Düsseldorf, 1988

2. J. Opfermann, a.o.: Lecture held at the TA-Seminar of the German Society for Thermal Analysis Osnabrück, 1989

3. L. Reich: Thermochimica Acta 7 (1973) 57-67

4. Krien: Mitteilung des BICT 1976, Az 3.0-3/3960/76 unpublished